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Date

August 1, 2006

Full name of the translator Tomoko MAEDA

Signature of the translator Tomoko Maeda

Post Office Address Kitahama TNK Building 7-1, Dosho-machi
1-chome, Chuo-ku, Osaka-shi, Osaka 541-0045
Japan

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SPECIFICATION

ELECTROPLATING IN PRESENCE OF CO_2

TECHNICAL FIELD

The present invention relates to an environmental technology using CO_2 as an alternative to conventional solvent. More specifically, the present invention relates to a technique for improving the efficiency of electrochemical reaction by using CO_2 as a solvent, and an electroplating technique employing such technique.

BACKGROUND OF THE INVENTION

Because of manifestation of various environmental problems, techniques using CO_2 as a solvent instead of toxic organic solvents have been attracting public attention. If compounds can be handled in CO_2, the cost for treating waste water may be significantly reduced, and therefore the idea of putting a such technique to practical use has been receiving particular attention in dying, plating and like industries which suffer from high waste water treatment costs. Having this as a technical background, a technique wherein CO_2 and a metal salt-containing aqueous solution are suspended while stirring, and then electroplating is conducted is disclosed (Patent Document 1, and Non-Patent Documents 1 and 2).

According to the information disclosed in these documents, the technique disclosed therein provides plated films having excellent microthrowing and covering properties without pinholes and a highly increased hardness due to the small particle diameter of the crystals formed, and therefore this technique makes it possible to obtain plated films having a higher quality than known electroplating techniques.

However, we reexamined this technique in detail and found that, in order to obtain excellent plated films without pinholes, this technique requires severe restrictions on the

conditions for conducting plating, including the selection of a surfactant.

For example, a polyoxyethylene blockcopolymer or polyoxyethylene alkylether, which is a hydrocarbon-based surfactant, is used in this technique. These surfactants have a low surface activity in a CO_2-water system, and therefore a large amount of surfactant, i.e., 3 to 6 wt% of a metal salt-containing aqueous solution (hereunder referred to as a plating solution), is used (Patent Document 1 and Non-Patent Documents 1 and 2). Therefore, in order to put these techniques into practical use, problems in removing the surfactant and plating solution that adhere to the surface of the plated film and drying the surface of the plated film must be resolved.

Furthermore, because of its considerable water solubility, a large amount of the polyoxyethylene compound used is also dissolved in a plating solution. Therefore, separation between the CO_2 and the plating solution does not easily progress in the plating bath after plating. This causes the formation of many bubbles containing the surfactant and plating solution during postprocessing decompression, and the resultant bubbles enter pipes, etc., causing pipes to become clogged. This problem significantly reduces efficiency in terms of throughput when such techniques are put into practical use.

These surfactants are required to have chemical stability under electrochemical conditions in a plating bath; however, no full examination has been conducted concerning this stability until now.

Heretofore, a very limited number of surfactants have been known to function in CO_2 (Patent Document 2, and Non-Patent Document 3).

Furthermore, concerning this supercritical plating technique, no information exists regarding the relationship between the type of surfactant used and the plating ease or resulting plated film.

[Patent Document 1] WO02/16673

[Patent Document 2] Japanese Unexamined Patent Publication No.10-36680

[Non-Patent Document 1] Yoshida, et al., MONTHLY MATERIAL STAGE, Vol.1, No.9, 2001, page 70

[Non-Patent Document 2] Yoshida, et al., Surface and Coatings Technology, Vol.173, 2003, page 285

[Non-Patent Document 3] Ohtake, et at., Hyomen (Surface), 2002, Vol. 40, page 353

DISCLOSURE OF THE INVENTION

[Problem to be Solved by the Invention]

An object of the present invention is to provide a technique that can improve the efficiency of electrochemical reaction using CO_2 as a solvent, and an electroplating technique employing such a technique.

[Means for Solving the Problem]

Considering the mechanism in which an electrochemical reaction occurs by forming an emulsion or turbid condition with CO_2 and a metal salt-containing aqueous solution, which do not inherently mix with each other, the present inventors conducted an examination by using a compound having a CO_2-affinitive moiety. As a result, when anionic surfactants were used, insoluble salts were formed in the plating solution and plating could either not be conducted or resulted in clogged pipes even if plating could be barely conducted. When cationic surfactants were used, no plated film was formed. In contrast, when nonionic compounds were used, plating was satisfactorily conducted. Furthermore, in order to apply this technique to electroplating conducted in CO_2, the present inventors reviewed a technique for forming a film in a plating bath, thus accomplishing the below mentioned inventions.

1. A method for conducting electroplating in the presence of CO_2 and a metal salt-containing aqueous solution, the CO_2 being liquid, subcritical or supercritical, the method further comprising a step of adding a nonionic compound having a CO_2-

affinitive moiety to a system wherein the aqueous solution and CO_2 coexist, the CO_2-affinitive moiety being at least one member selected from the group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

(2) fluorine-containing alkyl groups in which some or all of the hydrogen atoms are substituted by fluorine;

(3) fluorine-containing polyether groups in which some or all of the hydrogen atoms are substituted by fluorine; and

(4) dialkylsiloxy groups.

2. The method according to Item 1, wherein the nonionic compound is an ether-based or ester-based compound.

3. The method according to Item 1, wherein the nonionic compound is an alcohol-based compound.

4. The method according to Item 1, wherein the nonionic compound is a fluorinated hydrocarbon.

5. The method according to Item 1, wherein the nonionic compound is a polyalkylsiloxane.

6. The method according to Item 1, wherein the nonionic compound is a fluorine-containing polymer.

7. A plating bath comprising a metal salt-containing aqueous solution, CO_2, and a nonionic compound having a CO_2-affinitive moiety, the CO_2 being liquid, subcritical or supercritical, the CO_2-affinitive moiety being at least one member selected from the group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

(2) fluorine-containing alkyl groups in which some or all of the hydrogen atoms are substituted by fluorine;

(3) fluorine-containing polyether groups in which some or all of the hydrogen atoms are substituted by fluorine; and

(4) dialkylsiloxy groups.

8. An additive for use in electroplating conducted in the presence of liquid, subcritical or supercritical CO_2, the additive comprising a nonionic compound having a CO_2-affinitive moiety,

the CO_2-affinitive moiety being at least one member selected from the group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

(2) fluorine-containing alkyl groups in which some or all of the hydrogen atoms are substituted by fluorine;

(3) fluorine-containing polyether groups in which some or all of the hydrogen atoms are substituted by fluorine; and

(4) dialkylsiloxy groups.

9. A method for preprocessing conducted before plating comprising the step of degreasing and washing a plating substrate prior to plating using a nonionic compound having a CO_2-affinitive moiety,

the CO_2-affinitive moiety being at least one member selected from the group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

(2) fluorine-containing alkyl groups in which some or all of the hydrogen atoms are substituted by fluorine;

(3) fluorine-containing polyether groups in which some or all of the hydrogen atoms are substituted by fluorine; and

(4) dialkylsiloxy groups.

10. A method for postprocessing conducted after plating comprising the step of washing a plated film after plating using a nonionic compound having a CO_2-affinitive moiety, the CO_2-

affinitive moiety being at least one member selected from the group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

(2) fluorine-containing alkyl groups in which some or all of the hydrogen atoms are substituted by fluorine;

(3) fluorine-containing polyether groups in which some or all of the hydrogen atoms are substituted by fluorine; and

(4) dialkylsiloxy groups.

11. A plated film having

(1) per cm^2, not more than one pinhole having a diameter of at least 1 μm;

(2) a film thickness of not more than 1 μm; and

(3) a plated film surface roughness of not greater than 10 nm.

12. The method according to Item 1, wherein the nonionic compound used is (CO_2-affinitive moiety)-X- or X-(CO_2-affinitive moiety)-X- of 1) or 2) below respectively:

1) $F-(CF_2)_q-(OCF_3F_6)_m-(OC_2F_4)_n-(OCF_2)_o-(CH_2)_p-X-$, or

2) $-X-(CH_2)_p-(CF_2O)_o-(C_2F_4O)_n-(C_3F_6O)_m-(CF_2)_q-(OC_3F_6)_m-(OC_2F_4)_n-(OCF_2)_o-(CH_2)_p-X-$,

wherein m, n, o, p, and q are integers not smaller than 0, m and n are integers from 0 to 15 but not both 0, $n + m \leq 20$, o = 0 to 20, p = 0 to 2, and q = 1 to 10; the sequence of the repeating units not being fixed; $-(OC_3F_6)_m-$ represents $-(OCF_2CF_2CF_2)_m-$ or $-(OCF(CF_3)CF_2)_m-$, and $-(OC_2F_4)_n-$ represents $-(OCF_2CF_2)_n-$ or $-(OCF(CF_3))_n-$, and

each X may be the same or different, and represents a single bond, or O, S, NH, NR (R^a: alkyl group), C=O, C(O)O, OC(O), C(O)S, SC(O), C(O)NH, $C(O)NR^a$ (R^a: alkyl group), NH(O)C, NR(O)C, CH_2, CHR^a, CR^a_2 (R^a: alkyl group), SO_2NH, or $NHSO_2$.

13. The method according to Item 1, wherein the

nonionic compound is one of 1) to 3):

1) $F-(CF_2)_q-(OC_3F_6)_m-(OC_2F_4)_n-(OCF_2)_o-(CH_2)_pX-R_h$,

2) $F-(CF_2)_q-(OC_3F_6)_m-(OC_2F_4)_n-(OCF_2)_o-(CH_2)_pX-R_h-X-(CH_2)_p-(CF_2O)_o-(C_2F_4O)_n-(C_3F_6O)_m-(CF_2)_q-F$, and

3) $R_h-X(CH_2)_p-(CF_2O)_o-(C_2F_4O)_n-(C_3F_6O)_m-(CF_2)_q-(OC_3F_6)_m-(OC_2F_4)_n-(OCF_2)_o-(CH_2)_pX-R_h$,

wherein m, n, o, p, and q are integers not smaller than 0, m and n are integers from 0 to 15 but not both 0, $n + m \leq 20$, o = 0 to 20, p = 0 to 2, and q = 1 to 10; the sequence of the repeating units not being fixed; $-(OC_3F_6)_m-$ represents $-(OCF_2CF_2CF_2)_m-$ or $-(OCF(CF_3)CF_2)_m-$, and $-(OC_2F_4)_n-$ represents $-(OCF_2CF_2)_n-$ or $-(OCF(CF_3))_n-$, and

each X may be the same or different, and represents a single bond, or O, S, NH, NR (R^a: alkyl group), C=O, C(O)O, OC(O), C(O)S, SC(O), C(O)NH, C(O)NR^a (R^a: alkyl group), NH(O)C, NR(O)C, CH_2, CHR^a, CR^a_2 (R^a: alkyl group), SO_2NH, or $NHSO_2$, and each R_h is a hydrophilic moiety and a straight or branched chain hydrocarbon group that may contain hetero atoms.

14. The method according to Item 13, wherein R_h is a polyoxyalkylene group.

15. The method according to Item 13, wherein the nonionic compound comprises a CO_2-affinitive moiety whose number of carbon atoms is the same as or greater than that of the R_h group.

16. The method according to Item 1, wherein the nonionic compound comprises (CO_2-affinitive moiety)-X- or X-(CO_2-affinitive moiety)-X- of 1) or 2) below respectively:

1) $Y-(CF_2)_{m1}-(CH_2)_{n1}-X$, or

2) $X-(CH_2)_{n1}-(CF_2)_{m1}-(CH_2)_{n1}-X$,

wherein Y is F or H, each X may be the same or different and represents one member selected from the group consisting of COO, O, S, CONH, NHCO, SO_2NH, and $NHSO_2$, m1 is an

integer from 3 to 20, and each n1 may be the same or different and represents an integer from 0 to 2.

17. The method according to Item 16, wherein the nonionic compound is one of 1) to 3) below respectively:

1) $Y-(CF_2)_{m1}-(CH_2)_{n1}-X-R_h$,

2) $Y-(CF_2)_{m1}-(CH_2)_{n1}-X-R_h-X-(CH_2)_{n1}-(CF_2)_{m1}-Y$, or

3) $R_h-X-(CH_2)_{n1}-(CF_2)_{m1}-(CH_2)_{n1}-X-R_h$,

wherein Y is F or H, each X may be the same or different and represents one member selected from the group consisting of COO, O, S, CONH, NHCO, SO_2NH, and $NHSO_2$, each m1 may be the same or different and represents an integer from 3 to 20, each n1 may be the same or different and represents an integer from 0 to 2, and each R_h is a hydrophilic moiety and straight or branched chain hydrocarbon group that may contain hetero atoms.

18. The method according to Item 17, wherein R_h is a polyoxyalkylene group.

19. The method according to Item 17, wherein the nonionic compound comprises a CO_2-affinitive moiety whose number of carbon atoms is the same as or greater than that of each R_h group.

[Effect of the Invention]

In the present invention, the efficiency of an electroplating reaction can be improved and excellent metal films can be formed by using a nonionic compound having a CO_2-affinitive moiety, the nonionic compound having an excellent ability to emulsify CO_2 with an aqueous solution of an electrolyte (e.g., metal salt), which is a plating solution, having an excellent ability to remove or defoam bubbles formed during operations, and having a preferable wettability between a substrate, plating solution and CO_2. Furthermore, the present invention can simplify the preprocessing and postprocessing conducted before and after

plating and significantly improve throughput.

Use of the nonionic compound of the present invention achieves prompt separation between carbon dioxide and a metal-containing aqueous solution after stirring. This reliably prevents the problems of known techniques, such as bubbles of a metal-containing aqueous solution and carbon dioxide entering pipes and metal salts clogging pipes.

Furthermore, because the nonionic compound of the present invention exhibits a cleaning ability in supercritical carbon dioxide, it is effective for degreasing conducted prior to plating and washing conducted after plating. Therefore, the present invention greatly contributes to reducing alkaline and acidic waste liquids produced during preprocessing and metal waste liquids produced during washing in postprocessing, which are serious problems in prior art techniques.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates an apparatus as used in the Examples of the present invention.

Fig. 2 shows images of the plated film obtained in Example 1 taken using a scanning electron microscope.

Fig. 3 shows images of the plated film obtained in Example 2 taken using a scanning electron microscope.

Fig. 4 shows images of the plated film obtained in Example 3 taken using a scanning electron microscope.

Fig. 5 shows images of the plated film obtained in Example 4 taken using a scanning electron microscope.

Fig. 6 shows images of the plated film obtained in Example 5 taken using a scanning electron microscope.

Fig. 7 shows images of the plated film obtained in Example 6 taken using a scanning electron microscope.

Fig. 8 shows images of the plated film obtained in Example 7 taken using a scanning electron microscope.

Fig. 9 shows images of the plated film obtained in Example 8 taken using a scanning electron microscope.

Fig. 10 shows images of the plated film obtained in Example 9 taken using a scanning electron microscope.

Fig. 11 shows images of the plated film obtained in Example 10 taken using a scanning electron microscope.

Fig. 12 shows images of the plated film obtained in Example 11 taken using a scanning electron microscope.

Fig. 13 shows images of the plated film obtained in Example 12 taken using a scanning electron microscope.

Fig. 14 shows images of the plated film obtained in Example 13 taken using a scanning electron microscope.

Fig. 15 shows an image of the plated film obtained in Example 15 taken using a scanning electron microscope. (magnification of 500 times).

Fig. 16 show cross-sectional images of the plated film obtained in Reference Example taken by an SEM (magnifications of 30000 times and 10000 times).

Fig. 17 shows images of the plated film obtained in Comparative Example 1 taken using a scanning electron microscope.

Fig. 18 shows images of the plated film obtained in Comparative Example 2 taken using a scanning electron microscope.

[Explanation of numerical symbols]

1 carbon dioxide cylinder
2 valve
3 liquid feeding pump
4 thermostat
5 stirrer
6 rotor
7a electrode (anode)
7b electrode (cathode)
8 high-pressure container
9 power source for plating
10 pressure regulator

BEST MODE FOR CARRYING OUT THE INVENTION

When an electrochemical reaction is conducted in CO_2, it

is preferable, by using a nonionic compound having a CO_2-affinitive moiety, that CO_2 and a plating solution, which do not inherently mix with each other, be made to form an emulsion (O/W type micelle) or turbid condition only when stirred, and that the CO_2 and plating solution separate from each other at a desired rate when stirring is stopped. In addition, the ability to quickly remove or defoam the bubbles of hydrogen and like gasses formed on a substrate during the plating operation is very important for obtaining plated films without pinholes. Furthermore, during formation of a plated film, by controlling the wettability between the substrate, plating solution and CO_2, surface roughness of the plated film caused by micelles composed of plating solution can be suppressed.

The present inventors concluded that, in order to obtain such properties, having affinity for CO_2 as well as a certain degree of hydrophilicity is important, and therefore using a compound that does not contain any group bearing an electrical charge (i.e., is nonionic) but has a CO_2-affinitive moiety would be effective for achieving this object.

The present inventors concretely examined the plating operation as described below and found that only nonionic compounds exhibit excellent abilities. In contrast, when an anionic or cationic surfactant was used, no plated film was formed or serious problems arose during the operation (see Comparative Examples).

In other words, due to their high solubility in CO_2, the nonionic compounds effective in the present invention have the ability to effectively disperse CO_2 in the plating solution or to form a turbid condition or emulsion, to readily remove or defoam the bubbles formed on a substrate during a plating operation, and to provide preferable wettability between the plating solution, CO_2, and substrate.

The expression of preferable wettability, which is an essential property, is attributable to the above-mentioned nonionic compounds, and the most preferable compounds can be

selected considering various parameters required of the surfactant.

A preferable embodiment of the present invention is a nonionic compound having a CO_2-affinitive moiety comprising a CO_2-affinitive moiety and a hydrophilic moiety (a moiety having a low affinity for CO_2). In this embodiment, these two moieties may be linked to each other through a linking group X.

Regarding CO_2-affinitive moiety, examples of (1) homopolymers, bicopolymers and tricopolymers selected from the group consisting of polyoxypropylene, polyoxybutylene and polyoxyethylene include polyoxypropylenes, polyoxybutylenes, polyoxyethylenes, polyoxyethylene-polyoxypropylene copolymers, polyoxyethylene-polyoxybutylene copolymers, polyoxypropylene-polyoxybutylene copolymers, and polyoxyethylene-polyoxypropylene-polyoxybutylene copolymers. Such copolymers may be random copolymers, block copolymers, and graft copolymers; however, block copolymers are preferable.

The nonionic compound used in the present invention comprises at least one CO_2-affinitive moiety (R_f), and it may be a compound consists of a CO_2-affinitive moiety (R_f), or a compound comprising a CO_2-affinitive moiety (R_f) and a hydrophilic moiety (R_h) linked to each other through a linking group (X).

In more preferable embodiment of the present invention, the nonionic compound having a CO_2-affinitive moiety of the present invention has a structure such that a CO_2-affinitive moiety (R_f) and a hydrophilic group (R_h) are linked to each other through a suitable linking group (X)(wherein X represents a single bond, O, S, NH, NR (R^a: alkyl group), C=O, C(O)O, OC(O), C(O)S, SC(O), C(O)NH, C(O)NR^a (R^a: alkyl group), NH(O)C, NR(O)C, CH_2, CHR^a, $CR^a{}_2$(R^a: alkyl group), SO_2NH, or $NHSO_2$); an alkylene group (A) having a straight or branched chain that may be fluorinated (e.g., $(CH_2)_m$, $(CF_2)_n$, $CF(CF_3)$, $(CF_2)_n(CH_2)$, etc.) may lie between R_f and X and/or between R_h and X.

The method of the present invention is such that electroplating is conducted in the presence of a metal salt-

containing aqueous solution and CO_2. The method is characterized in that the CO_2 is liquid, subcritical or supercritical, and a nonionic compound having a CO_2-affinitive moiety is added to the system in which the aqueous solution and CO_2 coexist. Here, "a nonionic compound having a CO_2-affinitive moiety is added to the system in which the aqueous solution and CO_2 coexist" means that electroplating is conducted using a plating solution containing three components, i.e., CO_2 (the first component), a metal salt-containing aqueous solution (the second component), and a nonionic compound (the third component). The order of adding these three components is not fixed. For example, a nonionic compound may be added to a plating solution comprising CO_2 and a metal salt-containing aqueous solution to obtain a plating solution comprising the three components. It is also possible to obtain a plating solution comprising the three components by mixing a nonionic compound with CO_2 in advance and adding a metal salt-containing aqueous solution to the mixture. Alternatively, a metal salt-containing aqueous solution and a nonionic compound may be mixed in advance and CO_2 may be added to the mixture to obtain a plating solution comprising the three components.

The CO_2-affinitive moiety (R_f) is at least one member selected from the group consisting of:

(1) homopolymers, bicopolymers and tricopolymers of polyoxypropylene, polyoxybutylene and/or polyoxyethylene;

(2) fluorine-containing alkyl groups in which some or all of the hydrogen atoms are substituted by fluorine;

(3) fluorine-containing polyether groups; and

(4) dialkylsiloxy groups.

A particularly preferable CO_2-affinitive moiety is one of 1) to 4) below:

1) $F-(CF_2)_q-(OCF_3F_6)_m-(OC_2F_4)_n-(OCF_2)_o-(CH_2)_p-$,

2) $-(CH_2)_p-(CF_2O)_o-(C_2F_4O)_n-(C_3F_6O)_m-(CF_2)_q-(OC_3F_6)_m-(OC_2F_4)_n-(OCF_2)_o-(CH_2)_p-$

wherein m, n, o, p, and q are as defined above,

3) $Y-(CF_2)_m-(CH_2)_n-$, and

4) $-(CH_2)_n-(CF_2)_m-(CH_2)_n-$

wherein m, n, and Y are as defined above.

Examples of hydrophilic moieties (R_h) include compounds that do not contain any groups bearing electrical charges therein but contain at least one group selected from hydrocarbon, (poly)ether, and hydroxy groups (alcohols).

R_h is a straight or branched chain hydrocarbon group that may incorporate a heteroatom (e.g., oxygen, nitrogen, or sulfur atom) therein. Preferable R_h is a polyoxyalkylene group. Examples of polyoxyalkylene groups include polyoxypropylene, polyoxybutylene polyoxyethylene and like polyether groups. Some polyoxyalkylene groups having a certain chain length also function as CO_2-affinitive groups. Therefore, it is preferable that a polyoxyalkylene group functioning as R_h has a chain length such that the polyoxyalkylene group is not CO_2-affinitive but rather is hydrophilic (e.g., having 1 to 15 repeating units when R_f is $F-(CF(CF_3)CF_2O)_nCF(CF_3))$.

Examples of nonionic compounds having a CO_2-affinitive moiety (R_f) and hydrophilic moiety (R_h) are as below:

R_f-X-R_h,

$R_f-A-X-R_h$,

$R_f-X-A-R_h$,

$R_h-X-R_f-X-R_h$, and

$R_f-X-R_h-X-R_f$,

wherein R_f, R_h, and X are as defined above, and A represents a straight or branched chain alkylene group that may be fluorinated.

The compound effective in the present invention is a nonionic compound having a CO_2-affinitive moiety. In order to obtain further higher quality plated films, keeping a preferable balance between the CO_2-affinitive moiety (R_f) and hydrophilic group (R_h) is important. Such a balance can be expressed by the number of carbons of each group (i.e., R_f to R_h), and the ratio thereof is preferably as below. When the hydrophilic moiety is a hydrocarbon, $R_f : R_h$ is preferably 20 : 1 to 1 : 2 (10 : 1 to 1 :

1 is particularly preferable). When the hydrophilic moiety is an ether-containing group, R_f : R_h is preferably 20 : 1 to 1 : 1 (5 : 1 to 2 : 1 is particularly preferable).

Note that when the nonionic compound has two R_h groups or two R_f groups, the number of carbons thereof means the total number of carbons of the two R_h or R_f groups.

Usually, fluorinated compounds function in CO_2 better than hydrocarbon-based compounds, and therefore, in the plating operation of the present invention, they significantly contribute to reducing the amount of added compound necessary to emulsify the CO_2 and the plating solution. Furthermore, because nonionic compounds having a CO_2-affinitive moiety have low water-solubilities, they are not easily soluble in plating solutions, and therefore the time necessary for separating CO_2 from the plating solution can be reduced. This shows that a nonionic compound having a CO_2-affinitive moiety is a more effective additive than known hydrocarbon-based surfactants.

Furthermore, it became clear that a nonionic compound having a CO_2-affinitive moiety achieves excellent function because of its adequate hydrophilic properties. In contrast, when a carboxylate, which is an anionic surfactant, was used, the carboxylate formed insoluble salts with the metal contained in the plating solution (an aqueous metal salt-containing solution), and this became an obstacle to forming desirable plated films and conducting postprocessing after plating. Furthermore, when sulfonate among anionic surfactants was used, micelles did not disappear in postprocessing as fast as when a nonionic compound was used (the plating solution separation was insufficient), and therefore pipes became clogged due to bubbles containing the plating solution. When a cationic surfactant such as an ammonium salt was used, although electricity flowed, a plated film was not formed, probably because the surfactant adhered to the cathode (see the Comparative Examples).

In one preferable embodiment of the present invention, ether-based compounds, ester-based compounds, alcohol-based

compounds, polyalkylsiloxanes, fluorinated hydrocarbons, and fluorine-containing polymer compounds are exemplified as nonionic compounds having CO_2-affinitive moieties. Among these, ether-based and ester-based compounds are particularly preferable. In particular, fluorine-containing compounds exemplified in 1) to 6) below exhibit excellent effects:

1) $F-(CF_2)_q-(OCF_3F_6)_m-(OC_2F_4)_n-(OCF_2)_o-(CH_2)_p-X-R_h$,

2) $F-(CF_2)_q-(OC_3F_6)_m-(OC_2F_4)_n-(OCF_2)_o-(CH_2)_pX-R_h-X-(CH_2)_p-(CF_2O)_o-(C_2F_4O)_n-(C_3F_6O)_m-(CF_2)_q-F$,

3) $R_h-X(CH_2)_p-(CF_2O)_q-(C_2F_4O)_n-(C_3F_6O)_m-(CF_2)_q-(OC_3F_6)_m-(OC_2F_4)_n-(OCF_2)_o-(CH_2)_p-X-R_h$,

wherein m, n, o, p, q, X and R_h are as defined above, the sequence of the repeating units not being fixed; $-(OC_3F_6)_m-$ represents $-(OCF_2CF_2CF_2)_m-$ or $-(OCF(CF_3)CF_2)_m-$, and $-(OC_2F_4)_n-$ represents $-(OCF_2CF_2)_n-$ or $-(OCF(CF_3))_n-$),

4) $Y-(CF_2)_{m1}-(CH_2)_{n1}-X-R_h$,

5) $Y-(CF_2)_{m1}-(CH_2)_{n1}-X-R_h-X-(CH_2)_n-(CF_2)_m-Y$, and

6) $R_h-X-(CH_2)_n-(CF_2)_m-(CH_2)_n-X-R_h$

wherein m1 is an integer from 3 to 20, each n1 may be the same or different and represents an integer from 0 to 2, and X,Y, and R_h are as defined above.

Examples of the ether-based or ester-based compounds represented by the above structural formulae are compounds listed below. In addition to these compounds, various compounds may be effective as long as they satisfy the above-explained balance between the CO_2-affinitive moiety and hydrophilic moiety that can be determined by the number of carbons contained in each moiety. Such compounds make it possible to form excellent plated films, because of the wettability between the substrate, plating solution and CO_2, and because defoamation of hydrogen generated can be controlled in the most efficient manner.

$F-(CF(CF_3)CF_2O)_nCF(CF_3)COO(CH_2)_mCH_3$ (wherein n=1-15, and m=0-30)

$F-(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OOC(CH_2)_mCH_3$ (wherein n=1-15, and m=0-30)

$F-(CF(CF_3)CF_2O)_nCF(CF_3)CH_2O(CH_2)_mCH_3$ (wherein n=1-15, and m=0-30)

$F-(CF(CF_3)CF_2O)_nCF(CF_3)COO(CH_2CH_2O)_mCH_3$ (wherein n=1-15, and m=1-10)

$F-(CF(CF_3)CF_2O)_nCF(CF_3)COO(CH(CH_3)CH_2O)_mCH_3$ (wherein n=1-15, and m=1-10)

$F-(CF_2CF_2O)_nCF_2COO(CH_2)_mCH_3$ (wherein n=1-15, and m=0-30)

$F-(CF_2CF_2O)_nCF_2CH_2OOC(CH_2)_mCH_3$ (wherein n=1-15, and m=0-30)

$F-(CF_2CF_2O)_nCF_2CH_2O(CH_2)_mCH_3$ (wherein n=1-15, and m=0-30)

$F-(CF_2CF_2O)_nCF_2COO(CH_2CH_2O)_mCH_3$ (wherein n=1-15, and m=1-10)

$F-(CF_2CF_2O)_nCF_2COO(CH(CH_3)CH_2O)_mCH_3$ (wherein n=1-15, and m=1-10)

$CF_3(CF_2)_n-(CF_2CF_2O)_mCF_2COO(CH_2)_pCH_3$ (wherein n=1-8, m=1-15, and p=0-30)

$CF_3(CF_2)_n-(CF_2CF_2O)_mCF_2COO(CH_2CH_2O)_pCH_3$ (wherein n=1-8, m=1-15, and p=1-10)

$CF_3(CF_2)_n-(CF_2CF_2O)_mCF_2COO(CH(CH_3)CH_2O)_pCH_3$ (wherein n=1-8, m=1-15, and p=1-10)

$F-(CF_2CF_2CF_2O)_nCF_2CF_2COO(CH_2)_mCH_3$ (wherein n=1-15, and m=0-30)

$F-(CF_2CF_2CF_2O)_nCF_2CF_2CH_2OOC(CH_2)_mCH_3$ (wherein n=1-15, and m=0-30)

$F-(CF_2CF_2CF_2O)_nCF_2CF_2CH_2O(CH_2)_mCH_3$ (wherein n=1-15, and m=0-30)

$F-(CF_2CF_2CF_2O)_nCF_2CF_2COO(CH_2CH_2O)_mCH_3$ (wherein n=1-15, and m=1-10)

$F-(CF_2CF_2CF_2O)_nCF_2CF_2COO(CH(CH_3)CH_2O)_mCH_3$ (wherein n=1-15, and m=1-10)

$F-(CF_2CF_2CF_2O)_nCF_2CF_2CH_2O(CH_2CH_2O)_mCH_3$ (wherein n=1-15, and m=1-10)

$F-(CF_2CF_2CF_2O)_nCF_2CF_2CH_2O(CH(CH_3)CH_2O)_mCH_3$ (wherein n=1-15, and m=1-10)

$F-(CF(CF_3)CF_2O)_n(CF_2CF_2O)_mCF_2COO(CH_2)_pCH_3$ (wherein n=1-10, and m=1-10, p=0-30)

$F-(CF(CF_3)CF_2O)_n(CF_2CF_2O)_mCF_2COO(CH_2CH_2O)_pCH_3$ (wherein n=1-10, m=1-10, and p=1-10)

$F-(CF(CF_3)CF_2O)_n(CF_2CF_2O)_mCF_2COO(CH(CH_3)CH_2O)_pCH_3$ (wherein n=1-10, m=1-10, and p=1-10)

$F-(CF(CF_3)CF_2O)_nCF(CF_3)COO(CH_2CH_2O)_mOCO(CF_3)CF(OCF_2(CF_3)CF)_pF$ (wherein n=1-15, m=1-20, and p=1-15)

$F-(CF(CF_3)CF_2O)_nCF(CF_3)COO(CH_2)_mOCO(CF_3)CF(OCF_2(CF_3)CF)_pF$ (wherein n=1-15, m=1-30, and p=1-15)

$F-(CF(CF_3)CF_2O)_nCF(CF_3)COO(CH(CH_3)CH_2O)_mOCO(CF_3)CF(OCF_2(CF_3)CF)_pF$ (wherein n=1-15, m=1-20, and p=1-15)

$CH_3(CH_2)_nOCOCF(CF_3)(CF(CF_3)CF_2O)_mCF(CF_3)COO(CH_2)_pCH_3$

(wherein n=0-20, m=1-20, and p=0-20)

$CH_3(CH_2)_nOCOCF_2(OCF_2CF_2)_mOCF_2COO(CH_2)_pCH_3$

(wherein n=0-20, m=1-20, and p=0-20)

$CH_3(OCH_2CH_2)_nOCOCF(CF_3)(CF(CF_3)CF_2O)_mCF(CF_3)COO(CH_2CH_2O)_pCH_3$

(wherein n=1-10, m=1-20, and p=1-10)

$CH_3(OCH_2CH_2)_nOCOCF(CF_3)(OCF_2CF(CF_3))_m(CF_2)_n(CF(CF_3)CF_2O)_oCF(CF_3)COO(CH_2CH_2O)_pCH_3$

(wherein n=1-5, m+o=2-20, and p=1-10)

$CH_3(OCH_2CH_2)_nOCOCF_2(OCF_2CF_2)_mOCF_2COO(OCH_2CH_2)_pCH_3$

(wherein n=0-20, m=1-20, and p=0-20)

$CH_3(OCH_2CH(CH_3))_nOCOCF(CF_3)(CF(CF_3)CF_2O)_mCF(CF_3)COO(CH(CH_3)CH_2O)_pCH_3$

(wherein n=1-10, m=1-20, and p=1-10)

$F-(CF(CF_3)CF_2O)_nCF(CF_3)CH_2O(CH_2)_m(CF_2)_pCF_3$

(wherein n=1-15, m=1-10, and p=1-20)

$XCF_2(CF_2)_n(CH_2)_mO(CH_2)_pCH_3$

(wherein X=H, F, n=3-20, m=1-2, and p=1-20)

$XCF_2(CF_2)_n(CH_2)_mO(CH_2CH_2O)_pCH_3$

(wherein X=H, F, n=3-20, m=1-2, and p=1-10)

$XCF_2(CF_2)_n(CH_2)_mO(CH(CH_3)CH_2O)_pCH_3$

(wherein X=H, F, n=3-20, m=1-2, and p=1-10)

$XCF_2(CF_2)_n(CH_2)_mOOC(CH_2)_pCH_3$

(wherein X=H, F, n=3-20, m=1-2, and p=0-20)

$XCF_2(CF_2)_n(CH_2)_mCOO(CH_2)_pCH_3$

(wherein X=H, F, n=3-20, m=0-2, and p=0-20)

$XCF_2(CF_2)_n(CH_2)_mCOO(CH_2CH_2O)_pCH_3$

(wherein X=H, F, n=3-20, m=0-2, and p=1-10)

$XCF_2(CF_2)_n(CH_2)_mCOO(CH(CH_3)CH_2O)_pCH_3$

(wherein X=H, F, n=3-20, m=0-2, and p=1-10)

$CH_3(CH_2)_mOOC(CF_2)_nCOO(CH_2)_pCH_3$

(wherein m=0-20, n=1-20, and p=0-20)

$CH_3(OCH_2CH_2)_mOOC(CF_2)_nCOO(CH_2CH_2O)_pCH_3$

(wherein m=1-10, n=1-20, and p=1-10)

$CH_3(OCH_2CH(CH_3))_mOOC(CF_2)_nCOO(CH(CH_3)CH_2O)_pCH_3$

(wherein m=1-10, n=1-20, and p=1-10)

$CH_3(CH_2)_mCOO(CH(CH_3)CH_2O)_nCH_3$

(wherein m=1-20, and n=1-30), and

$CH_3(CH_2)_mO(CH(CH_3)CH_2O)_nCH_3$

(wherein m=1-20, and n=1-30)

Examples of preferable ether-based and ester-base partially fluorinated compounds include:

$F-(CF(CF_3)CF_2O)_nCF(CF_3)COO(CH_2)_mCH_3$

(wherein n=1-15, and m=0-30);

$F-(CF(CF_3)CF_2O)_nCF(CF_3)COO(CH_2CH_2O)_mCH_3$

(wherein n=1-15, and m=1-10);

$XCF_2(CF_2)_n(CH_2)_mO(CH_2)_pCH_3$

(wherein X=H, F, n=3-20, m=1-2, and p=0-20); and

$XCF_2(CF_2)_n(CH_2)_mCOO(CH_2)_pCH_3$

(wherein X=H, F, n=3-20, m=0-2, and p=0-20).

Examples of alcohol-based compounds, which are one exemplary embodiment of a nonionic compound, include:

$XCF_2(CF_2)_n(CH_2)_mOH$

(wherein X=H or F, n=3-20, and m=1-2)

$HOCH_2(CH_2)_m(CF_2)_n(CH_2)_pCH_2OH$

(wherein m=1-20, n=1-20, and p=1-20)

$F-(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OH$

(wherein n=1-15)

$HOCH_2(CF(CF_3)CF_2O)_nCF(CF_3)CH_2OH$

(wherein n=1-15)

$HOCH_2CF(CF_3)(CF(CF_3)CF_2O)_mCF(CF_3)CH_2OH$

(wherein m=1-20)

$F-(CF_2CF_2O)_mCF_2CH_2OH$

(wherein m=1-20)

$CF_3O-(CF_2CF_2O)_mCF_2CH_2OH$

(wherein m=1-20)

$HOCH_2(CF_2CF_2O)_mCF_2CH_2OH$

(wherein m=1-20)

$HOCH_2CF_2(OCF_2CF_2)_m(OCF_2)_nOCF_2CH_2OH$

(wherein n+m=1-20)

$F-(CF_2CF_2CF_2O)_mCF_2CF_2CH_2OH$

(wherein m=1-20)

$F-(CF(CF_3)CF_2O)_n(CF_2CF_2O)_mCF_2CH_2OH$
(wherein n=1-10,and m=1-10), and
$CF_3(CF_2)_n-(CF_2CF_2O)_mCF_2CH_2OH$
(wherein n=1-10, and m=1-10).

Examples of polyalkylsiloxanes, which are one exemplary embodiment of a nonionic compound, include:
$-(Si(CH_3)((CH_2)_3-(OCH_2CH_2)_p-OCH_3))_mO-(Si(CH_3)_2O)_n-$
(wherein m=10-100, n=10-100, and p=1-10),
$-(Si(CH_3)((CH_2)_3-(OC_3H_6)_p-OCH_3))_mO-(Si(CH_3)_2O)_n-$
(wherein m=10-100, n=10-100, and p=1-10),
$CH_3O-(Si(CH_3)-(O_2C(CH_2)_pCH_3))_mO-(Si(CH_3)_2O)_n-CH_3$
(wherein m=10-100, n=10-100, and p=1-20),
$CH_3O-(Si(CH_3)_2)_mO-(Si(CH_3)_2O)_n-CH_3$
(wherein m=10-100, and n=10-100), and
$R_3Si-O-(SiR_2O-)_n-(SiR(R_h)O-)_m-SiR_3$
(wherein $-(SiR_2O-)_n$ and $(SiR(R_h)O-)_m$ are random or block polymer units, R is a C_1-C_4 alkyl group, R_h is as defined above, n:m is 10:1 to 1:1, and n=10-500),
R_2R_h $Si-O-(SiR_2O-)_n-(SiR_2R_h)$
(wherein n:m is 10:1 to 1:1, n=10-500, R is a C_1-C_4 alkyl group, and R_h is as defined above), and
$R_3Si-O-(SiR_2O-)_n-R_h-(SiR_2O-)_m-SiR_3$
(wherein n:m is 10:1 to 1:1, n=10-500, R is a C_1-C_4 alkyl group, and R_h is as defined above).

An example of a fluorinated hydrocarbon, which is one exemplary embodiment of nonionic compound, is as below:
$X(CF_2)_m(CH_2)_nH$ (wherein X=H, or F, n=3-20, and m=1-20).

Examples of fluorine-containing polymers, which are one exemplary embodiment of a nonionic compound, include:
$-(CH_2CH(CO_2CH_2CH_2(CF_2)_mCF_3))_n-$
(wherein m=2-8, and n=5-100),
$-(CH_2CH(OCH_2CH_2OCOCH_2CH_2(CF_2)_mCF_3))_n-$
(wherein m=2-8, and n=5-100),
$-(CH_2CH(OCH_2CH_2OCOCF(CF_3)(OCF_2CF(CF_3))_mF)_n-$
(wherein m=1-15, and n=5-100),

$-(CH_2CH(CH_2OCH_2CH_2(CF_2)_mCF_3)O)_n-$

(wherein m=2-8, and n=5-100), and

$-(CH_2CH(CH_2OCH_2CF(CF_3)(OCF_2CF(CF_3))_mF)_n-$

(wherein m=1-15, and n=5-100).

When conducting electroplating, the ratio by volume of CO_2 (supercritical, subcritical or liquid) to the plating solution (metal salt-containing aqueous solution) used in the present invention is generally plating solution : CO_2 = 5 : 95 to 95 : 5, preferably 10 : 90 to 80 : 20, and more preferably 20 : 80 to 60 : 40.

Nonionic compounds having CO_2-affinitive moieties used in the present invention are commercially available or can be readily produced by persons of skill in the art.

The amount of nonionic compound having a CO_2 affinitive moiety used in the present invention is generally about 0.001 to 10 wt%, preferably about 0.01 to 5 wt%, and more preferably about 0.1 to 1 wt% of the metal salt-containing aqueous solution. Because of its excellent abilities, the amount of nonionic compound having a CO_2-affinitive moiety necessary for achieving satisfactory results is very small, for example, about 0.1 wt%. The nonionic compound having a CO_2 affinitive moiety is superior to hydrocarbon-based compounds in this respect as well.

It is also possible to further add organic solvents (co-solvent) as follows. Examples of usable organic solvents include methanol, ethanol, propanol, butanol, pentanol and like alcohols; acetone and like ketones; acetonitrile; ethyl acetate and like esters; ethyl ether and like ethers; and chlorofluorocarbons, methylene chloride, chloroform and like halides. Among these, low molecular weight low toxicity compounds are preferable.

In the present invention, CO_2 is used in a form of liquid, subcritical, or supercritical. Because the thus-obtained system is biphasic, agitation is necessary. Such agitation includes magnetic stirring, mechanical stirring, and mixing using ultrasonic irradiation, etc.

In stirring, the specific number of revolutions depends on the type of nonionic compound having a CO_2-affinitive moiety, the scale of the apparatus, and the method of stirring, and therefore it must be suitably selected during the actual operation.

The surfactant of the present invention promotes formation of excellent plated films by making mixing the plating solution with CO_2 easy, and stabilizing the micelles formed during the mixing procedure. Therefore, the effects of the surfactant of the present invention are not limited by the order of placing the surfactant, plating solution, and CO_2 in the apparatus, the method for mixing these components, and the agitation method. The Examples disclosed in the present specification were conducted using small-scale experimental methods; however, there are suitable ways of mixing and/or stirring the components in large-scale experiments according to the scale, and therefore the most desirable method of introducing the surfactant should be considered for each operation. Such a method can be easily selected by a person having ordinary skill in the art. Regardless of how CO_2 is mixed with the plating solution, the surfactant of the present invention provides better plated films than when plating is conducted using hydrocarbon-based or ionic surfactants.

In this specification, in addition to electroplating itself, the concept of electroplating includes electrolytic oxidation, electrolytic reduction and like electrode reactions; electrochemical analysis, corrosion, corrosion prevention, and passivation of metals, etc.

The temperature of the electroplating reaction of the present invention is about 10 to 100°C.

The pressure is generally about 0.1 to 30 MPa, preferably about 1 to 20 MPa, and more preferably about 5 to 15 MPa.

When magnetic stirring or mechanical stirring is employed, the number of revolutions is generally 100 to 100000 rpm and preferably 400 to 1000 rpm, and when ultrasonic

irradiation is employed, the frequency may be, for example, 20 kHz to 10 MHz.

When electrolytic plating is conducted, an electrolyte, in particular an electrolyte containing one or more types of metal, is dissolved in an aqueous phase. Examples of metals contained in such electrolyte include Ni, Co, Cu, Zn, Cr, Sn, W, Fe, Ag, Cd, Ga, As, Cr, Se, Mn, In, Sb, Te, Ru, Rh, Pd, Au, Hg, Tl, Pb, Bi, Po, Re, Os, Ir, Pt, etc. Examples of electrolyte include aqueous chlorides, bromides, iodides and like halides of such metals; nitrates, sulfates, sulfamates, acetates and like organic salts of such metals; cyanides, oxides, hydroxides, and complex of such metals, etc.

It is also possible to form a semiconductor of an oxide film, a nitride film, etc., using the technique of the present invention as other electrochemical surface treatments.

By using the additive (nonionic compound) for electroplating of the present invention, defoamation (separation) of the turbid liquid of carbon dioxide and metal salt-containing aqueous solution after plating can be conducted rapidly.

For example, when the additive for electroplating of the present invention is used, the time from stopping stirring (stirring conducted at 10 MPa, 50°C, and 500 r.p.m.) to completion of defoamation is generally not longer than 10 minutes, and preferably not longer than 5 minutes.

The plated film obtained in the present invention has

(1) per cm^2, not more than one pinhole having a diameter of at least 1 μm;

(2) a film thickness of not more than 1 μm; and

(3) a plated film surface roughness of not greater than 10 nm.

Furthermore, the diameter of the metal particles of the plated film obtained in the present invention is naturally smaller than that obtained by using known plating techniques as well as smaller than that obtained by using supercritical CO_2 plating techniques wherein hydrocarbon-based surfactants are used.

It is reported that the diameter of crystals obtained by typical glossy plating is about 1 μm and that obtained by known supercritical plating techniques is about 100 nm (Yoshida et al, Surface and Coatings Technology, 2003, Vol. 173, page 285). In contrast, when the additive of the present invention is used, the diameter of the metal particles of the plated film is about 10 nm (see the Reference Example). Therefore, the metal film obtained in the present invention is very densely packed and expected to have high wear resistance. The quality of the metal film obtained in the present invention is almost equal to those of metal films obtained by chemical plating or dry processing, which are nonproductive and require large amounts of energy. The technique of the present invention can provide a method by which metal materials, which used to be provided by dry processing, despite its low productivity, can be obtained in a highly efficient manner.

Furthermore, because the plating can be conducted under conditions where the supercritical fluid has a low interfacial tension, the present invention can achieve the surface treatment of a base material with very small bumps and dips on which a plated film cannot be formed by conventional electrolytic plating techniques. Specifically, such a base material has a structure having a pattern width of the submicronic level and a high aspect ratio. Such a structure corresponds to those of materials used for semiconductors and MEMs. More specifically, the technique of the present invention can provide a plated film having a uniform thickness over bumps and dips with a pattern width of not greater than 1 μm and an aspect ratio of not smaller than 3. It is also possible to conduct wiring plating inside the via/trench structure of a semiconductor wafer.

Furthermore, the thickness of the plated film can be controlled at a level of several tens of nm by controlling the pressure and current density, and the proportion of carbon dioxide to the plating solution. Therefore, the present invention is very useful in material fields wherein a metal film having a

thickness of submicronic order, very small surface roughness, without pinholes, and a high corrosion resistance is required. Specific examples of such materials include those for fuel cells, nozzles for ink-jet printers, electronics industry materials such as magnetic heads, materials for internal combustion engines, and materials for press pumps.

Note that the plated film surface roughness can be measured by images taken using a scanning electron microscope.

Use of the surfactant of the present invention makes it possible to obtain a metal thin film with such high quality by supercritical plating.

Furthermore, because the nonionic compound of the present invention has a cleaning ability in supercritical carbon dioxide, it is effective in degreasing/washing in preprocessing conducted before plating and washing in postprocessing conducted after plating. Specifically, a plated film having as high a quality as that of the present invention can be formed, without prior degreasing and washing of the substrate, by conducting electroplating after degreasing and washing a substrate using a mixture of the nonionic compound and CO_2 (supercritical, subcritical or liquid), or by conducting degreasing, washing, and plating at the same time using a plating solution comprising the nonionic compound, CO_2 (supercritical, subcritical or liquid), and a metal salt-containing aqueous solution. The plating solution is removed from the surface of the thus-obtained plated film to such an extent that the film can be sufficiently functional without having to remove the plating solution using a large volume of water. In other words, formation of a plated film by electroplating and washing of the film can be conducted at the same time. In some cases, the film after plating may be washed (postprocessing) using a mixture of the nonionic compound and CO_2 (supercritical, subcritical or liquid). Therefore, the present invention significantly contributes to the reduction of alkaline or acid waste waters generated in preprocessing and metal-containing waste waters generated in washing in postprocessing,

which have been particular problems in prior art plating process.

Examples

The present invention is explained in detail with reference to Examples and Reference Examples; however, the present invention is not limited to these.

Example 1

Fig. 1 illustrates the apparatus used in the Examples of the present invention. In a 50 cm^3 high-pressure container 8 were placed 20 cm^3 of nickel plating bath (Watt bath comprising 280 g/L nickel sulfate, 60 g/L nickel chloride, 50 g/L boric acid, and a brightener (q.s.)) and 0.3 wt% of $F(CF(CF_3)CF_2O)_3CF(CF_3)COO(CH_2CH_2O)_2CH_3$ relative to the nickel plating bath. After attaching a degreased brass plate to the cathode and pure nickel plate to the anode (both having a surface area of 4 cm^2), the high-pressure container 8 was sealed, and then heated to 50°C in a thermostat 4. CO_2 was filled in the container using a liquid feeding pump 3 and pressure regulator 10 until the pressure reached 10 MPa. Nickel plating was conducted by stirring the CO_2-plating solution by rotating a rotor 6 at 500 rpm using a stirrer 5, and passing an electric current at 5 A/dm^2 for 6 minutes. After completion of electric current passage, the high-pressure container 8 was subjected to decompression, the cathode was removed and sufficiently washed with water, and the surface was observed using a scanning electron microscope (SEM). Fig. 2 shows scanning electron microscope photographs.

Example 2

Plating was conducted in the same manner as Example 1 except that $H(CF_2)_6COOCH_2CH_3$ was used as a nonionic compound having a CO_2-affinitive moiety.

Fig. 3 shows scanning electron microscope photographs.

Example 3

Plating was conducted in the same manner as Example 1 except that $F(CF_2)_6(CH_2)_{10}H$ was used as a nonionic compound having a CO_2-affinitive moiety.

Fig. 4 shows scanning electron microscope photographs.

Example 4

Plating was conducted in the same manner as Example 1 except that $F(CF_2)_7COOCH_2CH_3$ was used as a nonionic compound having a CO_2-affinitive moiety.

Fig. 5 shows scanning electron microscope photographs.

Example 5

Plating was conducted in the same manner as Example 1 except that $F(CF(CF_3)CF_2O)_4CF(CF_3)COOCH_3$ was used as a nonionic compound having a CO_2-affinitive moiety.

Fig. 6 shows scanning electron microscope photographs.

Example 6

Plating was conducted in the same manner as Example 1 except that $F(CF_2)_7COO(CH_2)_5CH_3$ was used as a nonionic compound having a CO_2-affinitive moiety.

Fig. 7 shows scanning electron microscope photographs.

Example 7

Plating was conducted in the same manner as Example 1 except that $F(CF(CF_3)CF_2O)_2CF(CF_3)CH_2OH$ was used as a nonionic compound having a CO_2-affinitive moiety.

Fig. 8 shows scanning electron microscope photographs.

Example 8

Plating was conducted in the same manner as Example 1 except that $F(CF(CF_3)CF_2O)_3CF(CF_3)COOCH_2CH_2OCH_3$ was used as a nonionic compound having a CO_2-affinitive moiety.

Fig. 9 shows scanning electron microscope photographs.

Example 9

Plating was conducted in the same manner as Example 1 except that $F(CF(CF_3)CF_2O)_3CF(CF_3)COOC_6H_{13}$ was used as a nonionic compound having a CO_2-affinitive moiety.

Fig. 10 shows scanning electron microscope photographs.

Example 10

Plating was conducted in the same manner as Example 1 except that $F(CF(CF_3)CF_2O)_3$ $CF(CF_3)CO(OCH_2CH_2)_3OCOCF(CF_3)(OCF_2(CF_3)CF)_3F$ was used as a nonionic compound having a CO_2-affinitive moiety.

Fig. 11 shows scanning electron microscope photographs.

Example 11

Plating was conducted in the same manner as Example 1 except that $CH_3OCH_2CH_2OCCF_2(OCF_2CF_2)_6OCF_2COOCH_2CH_2OCH_3$ was used as a nonionic compound having a CO_2-affinitive moiety.

Fig. 12 shows scanning electron microscope photographs.

Example 12

Plating was conducted in the same manner as Example 1 except that $C_{12}H_{25}OCOCF(CF_3)O(CF_2(CF_3)CFO)_m-(CF_2)_5-(OCF(CF_3)CF_2)_m-OCF(CF_3)COOC_{12}H_{25}$ (wherein $m = 3$ to 5) was used as a nonionic compound having a CO_2-affinitive moiety.

Fig. 13 shows scanning electron microscope photographs.

Example 13

In a 50 cm^3 high-pressure container 8 were placed 20 cm^3 of an acid gold plating bath (comprising 10 g/L potassium gold cyanide and 90 g/L citric acid) and 0.3 wt% of $F(CF(CF_3)CF_2O)_3CF(CF_3)COO(CH_2CH_2O)_2CH_3$ relative to the plating bath. After attaching a nickel-plated brass plate to the cathode and platinum-plated titanium plate to the anode (both having a surface area of 4 cm^2), the high-pressure container 8 was sealed,

and then heated to 40°C in a thermostat 4. CO_2 was filled in the container using a liquid feeding pump 3 and pressure regulator 10 until the pressure reached 10 MPa. Gold plating was conducted by stirring the CO_2-plating solution by rotating a rotor 6 at 500 rpm using a stirrer 5 and passing an electric current at 2 A/dm^2 for 2 minutes. After completion of electric current passage, the high-pressure container 8 was subjected to decompression, the cathode was removed and sufficiently washed with water, obtaining an excellent gold-plated film. Fig. 14 shows scanning electron microscope photographs (magnification: 500 times).

Example 14

In a 50 cm^3 high-pressure container 8 were placed 20 cm^3 of copper sulfate plating bath (comprising 200 g/L copper sulfate pentahydrate, 50 g/L sulfuric acid, and q.s. hydrochloric acid) and 0.3 wt% of $F(CF(CF_3)CF_2O)_3CF(CF_3)COO(CH_2CH_2O)_2CH_3$ relative to the plating bath. After attaching a brass plate to the cathode and copper plate to the anode (both having a surface area of 4 cm^2), the high-pressure container 8 was sealed, and then heated to 50°C in a thermostat 4. CO_2 was filled in the bath using a liquid feeding pump 3 and pressure regulator 10 until the pressure reached 10 MPa. Copper plating was conducted by stirring the CO_2-plating solution by rotating a rotor 6 at 500 rpm using a stirrer 5 and passing an electric current at 5 A/dm^2 for 5 minutes. After completion of electric current passage, the high-pressure container 8 was subjected to decompression, the cathode was removed and sufficiently washed with water, obtaining an excellent copper plated film.

Example 15

In a 50 cm^3 high-pressure container 8 were placed 20 cm^3 of acid gold plating bath (comprising 0.10 mol/L palladium chloride, 4.00 mol/L potassium bromide, 0.10 mol/L potassium nitrate, 0.49 mol/L boric acid, 0.10 mol/L glycine, and 90 g/L citric acid) and 0.3 wt% of $F(CF(CF_3)CF_2O)_3CF(CF_3)COO(CH_2CH_2O)_2CH_3$

relative to the plating bath. After attaching a gold- and platinum-plated silver plate to the cathode and platinum plate to the anode (both having a surface area of 4 cm^2), the high-pressure container 8 was sealed, and then heated to 40°C in a thermostat 4. CO_2 was filled in the container using a liquid feeding pump 3 and pressure regulator 10 until the pressure reached 12 MPa. The CO_2-plating solution was sufficiently mixed and stirred by rotating a rotor 6 at 650 rpm for one hour using a stirrer 5. Palladium plating was conducted by passing an electric current at 1 A/dm^2 for 15 minutes. After completion of electric current passage, the high-pressure container 8 was subjected to decompression, the cathode was removed and sufficiently washed with water, obtaining an excellent palladium-plated film. Fig. 15 shows scanning electron microscope photographs.

Example 16

Nickel plating was conducted in the same manner as in Example 1 except that an untreated brass plate was attached to the cathode and pure nickel plate to the anode (both having a surface area of 4 cm^2). After completion of electric current passage, the high-pressure container 8 was subjected to decompression. The cathode was removed and the surface thereof was observed with the naked eye and using a scanning electron microscope (SEM). It was found that a plated film having almost the same quality as that of Example 1 was obtained. From this result, it became clear that by using the compound of the present invention in supercritical carbon dioxide, the preprocessing and postprocessing conducted before and after plating could be omitted.

Reference Example

A cross section of the plated film obtained in Example 8 was observed using an SEM. Fig. 16 shows the results as cross-sectional SEM images of magnifications of 10000 times or 30000 times. The crystal diameters were 7 to 12 nm, and the surface of

the plated film was very smooth. The variance of the thickness of the surface was about 10 nm. Because the thickness of the film was 1 μm, this suggests that controlling of the thickness to about 100 nm can be easily conducted.

Comparative Example 1

Plating was conducted in the same manner as in Example 1 except that 3 wt% of $CH_3(CH_2)_{12}(OCH_2CH_2)_8OH$ was used instead of the nonionic compound having a CO_2-affinitive moiety. Clogged pipes were observed during the postprocessing caused by formation of bubbles.

Fig. 17 shows scanning electron microscope photographs. From the SEM observations, it was clear that although no pinholes were formed in the plated film, the surface thereof was very rough compared when a nonionic compound having a CO_2-affinitive moiety was used.

Comparative Example 2

Using a plating solution having the same composition as that used in Example 1, plating was conducted without adding CO_2 (i.e., using a prior art plating technique).

Fig. 18 shows scanning electron microscope photographs. Large pinholes were observed.

Comparative Example 3

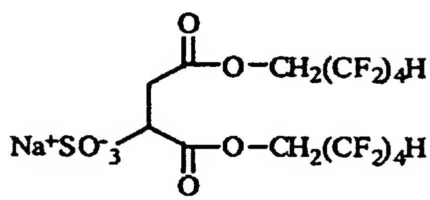
Plating was conducted in the same manner as in Example 1 except that $F(CF(CF_3)CF_2O)_{14}CF(CF_3)COO^-NH_4^+$ was used instead of the nonionic compound having a CO_2-affinitive moiety. Electric current did not flow, and formation of a plated film was not observed. A gel solution had formed in the apparatus after completion of the reaction.

Comparative Example 4

Plating was conducted in the same manner as in Example 1 except that a compound represented by Chemical Formula 1 below

was used instead of the nonionic compound having a CO_2-affinitive moiety.

[Chemical Formula 1]



Electric current flowed and plating could be conducted; however, bubbles formed when the plating solution was emulsified during the decompression in the postprocessing overflowed from the apparatus and entered the pipes.

Comparative Example 5

Plating was conducted in the same manner as in Example 1 except that $F(CF_2(CF_3)CF_2O)_3(CF_3)CFCONHCH_2CH_2N^+(CH_3)_3I^-$ was used instead of the nonionic compound having a CO_2-affinitive moiety. Electric current did not flow, and adhesion of a brown substance to the surface of the cathode was observed.

When the images of the surfaces of the films obtained in Examples 1 to 16 are compared to that of Comparative Example 1 (in which a hydrocarbon-based surfactant was used), the surfaces of the films obtained in Examples 1 to 16 clearly have no pinholes and smaller surface roughnesses, and therefore it can be said that excellent plated films were formed (from the SEM observations, it is clear that the surface roughnesses of Examples 1 to 16 are smaller than when a hydrocarbon-based compound was used). Furthermore, when a hydrocarbon-based surfactant was used, even though plating could be completed, troublesome postprocessing was required (Comparative Example 1).

When a fluorine-based surfactant was used, if it was an anionic compound, plating could not be completed or troublesome postprocessing was required, and if it was a cationic compound,

plating could not be completed. As described above, in this technique, remarkable differences are observed in the plated films attributable to the difference in the properties (structures) of the additives used. Accordingly, it became clear that by using the nonionic compound having a CO_2-affinitive moiety of the present invention, plated films with high quality can be formed by taking advantage of plating using liquid, subcritical or supercritical CO_2.